

An Intercomparison of Nitrogen-Containing Species in Nimbus 7 LIMS and SAMS Data

CHARLES H. JACKMAN, PAUL D. GUTHRIE, AND JACK A. KAYE

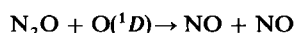
Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland

Nitrogen dioxide (NO_2) and nitric acid (HNO_3) distributions were derived with a two-dimensional time-dependent model using N_2O , CH_4 , and temperature measurements from the stratospheric and mesospheric sounder (SAMS) along with H_2O measurements from the limb infrared monitor of the stratosphere (LIMS) and O_3 measurements from the solar backscatter ultraviolet (SBUV) instrument. All three instruments (SAMS, LIMS, and SBUV) were aboard the Nimbus 7 satellite. The computed NO_2 and HNO_3 were compared with LIMS NO_2 and HNO_3 measurements. Calculated NO_2 is lower than the LIMS NO_2 in much of the lower stratosphere by about a factor of 4 or more. Differences in the upper stratosphere between derived NO_2 and LIMS NO_2 are within the photochemical uncertainties of the computation. Derived NO_2 is much larger than LIMS NO_2 at high latitudes in the upper stratosphere in December, indicating that dynamics and/or photochemistry in the atmosphere are different from those used in the model. Derived HNO_3 is in fairly good agreement with LIMS HNO_3 in the upper stratosphere. Derived and LIMS HNO_3 gradually become more different through the middle stratosphere and reach a fairly substantial disagreement in the lower stratosphere. The high-latitude maxima observed in LIMS HNO_3 are present at lower altitudes and at higher concentrations than those derived in the model computations. More significantly, the derived HNO_3 at polar latitudes is highest in the summer while LIMS HNO_3 is highest in the winter. Disagreements in the lower stratosphere between the computed and LIMS NO_2 and HNO_3 can only be reduced if two changes are made in the model computations: (1) additional lower stratospheric sources of odd nitrogen (other than $\text{N}_2\text{O} + \text{O}(^1D)$) are included and (2) a modified chemistry to allow the formation of HNO_3 at the expense of N_2O_5 is used.

INTRODUCTION

Odd nitrogen (N , NO , NO_2 , NO_3 , N_2O_5 , HNO_3 , HO_2NO_2 , and ClONO_2) in the middle atmosphere is quite important not only because of its influence on ozone, accounting for 50–80% of the total loss of ozone in the middle to lower stratosphere [Jackman *et al.*, 1986], but also because of its influence on the HO_x and Cl_x cycles (see, for example, Nicolet [1975a]). It has generally been assumed that nitrous oxide (N_2O) emitted at the ground is the predominant source of stratospheric odd nitrogen. Simultaneous global satellite measurements of O_3 , NO_2 , HNO_3 , H_2O , and temperature (by the limb infrared monitor of the stratosphere (LIMS) instrument on Nimbus 7), N_2O , CH_4 , and temperature (by the stratospheric and mesospheric sounder (SAMS) instrument on Nimbus 7), and O_3 (by the solar backscatter ultraviolet (SBUV) instrument on Nimbus 7) allow us the opportunity for the first time to test our global understanding of odd nitrogen chemistry and transport. In particular, we can determine whether the odd nitrogen levels implied by the SAMS data are consistent with the odd nitrogen amounts measured by LIMS.

We use the SAMS N_2O measurements together with a two-dimensional model to compute NO_2 and HNO_3 which can then be compared with LIMS NO_2 and HNO_3 (the LIMS HNO_3 data being modified by the scheme given by Jackman *et al.* [1985]). The N_2O molecule is probably the major precursor for odd nitrogen in the stratosphere [Crutzen, 1970; Nicolet, 1971; McElroy and McConnell, 1971]. The reaction



is assumed to provide about 90% of the odd nitrogen in the stratosphere [e.g., Jackman *et al.*, 1980]. Other sources of odd nitrogen have been suggested for the middle atmosphere such as galactic cosmic rays, lightning, solar proton events, precipitation by relativistic electrons, meteors, and the downflux of odd nitrogen from the thermosphere, but these other sources are assumed to contribute less than 10% of the total odd nitrogen to the stratosphere [see Jackman *et al.*, 1980]. As part of this study we have investigated the premise that N_2O is the major source of odd nitrogen in the stratosphere using a time-dependent two-dimensional model with N_2O and other significant gases constrained to satellite data.

Our premise of N_2O being the major source of odd nitrogen in the stratosphere is not universally accepted. Several years ago, Tuck [1976] indicated that lightning might be a large source as well. We discuss the impact of other nitrogen sources, such as lightning, on the stratospheric odd nitrogen distribution later in this paper.

TWO-DIMENSIONAL BACKGROUND ATMOSPHERE

We have used the two-dimensional model of Guthrie *et al.* [1984a], modified somewhat for this study. This model extends from 878.72 to 0.23 mbar and from 85°S to 85°N latitude. The nine fixed species in the model for this study are O_3 , H_2O , CH_4 , N_2O , CFCl_3 , CF_2Cl_2 , CO_2 , N_2 , and O_2 . The calculated species are O , $\text{O}(^1D)$, N , NO , NO_2 , NO_3 , N_2O_5 , HO_2NO_2 , HNO_3 , H , OH , HO_2 , Cl , ClO , HCl , HOCl , ClONO_2 , and H_2 . Since we use the model for time-dependent computations, it is necessary to find values for the nine fixed species at all levels in our model. Satellite measurements of species O_3 , H_2O , CH_4 , and N_2O are not available at all levels in our model. Some extrapolation is required to obtain concentrations for these species at other levels in the model, and we use some earlier two-dimensional results to complete the distributions of these species.

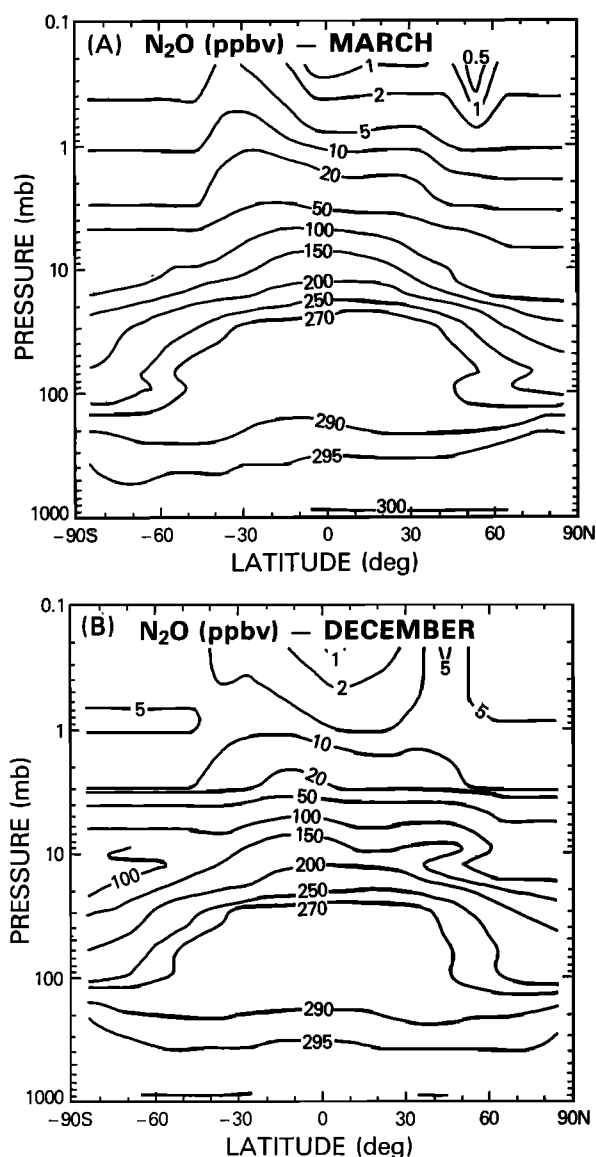
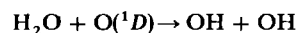


Fig. 1. N_2O distribution used for (a) March and (b) December in the two-dimensional model computations.

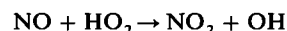
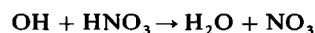
The O_3 was taken from the SBUV data of Nimbus 7. We use the data given by *McPeters et al.* [1984] as our basis. The SBUV O_3 is the most complete set of O_3 measurements, extending from about 500 to 0.17 mbar and over the entire year (the LIMS O_3 extends only from 100 to 0.1 mbar and exists for only seven months). We assume that below 500 mbar the O_3 mixing ratios are fixed to the SBUV O_3 mixing ratio data at 500 mbar. At latitudes during polar night we assume the O_3 is fixed to the SBUV O_3 data at the highest latitude for which there are data. The O_3 density and the calculated local ultraviolet flux should be good approximations to those of the real atmosphere. Ozone has a large effect on odd nitrogen species: (1) O_3 has a profound influence on the NO/NO_2 balance and (2) O_3 and HNO_3 absorb in overlapping wavelength regions [see *Froidevaux and Yung, 1982; Brasseur et al., 1983*]. Also, because the modeled ozone tends to be different from the measured ozone, especially in the upper stratosphere and above (see, for example, *Wofsy [1978], Solomon et al. [1983]*, and other references in the work by *Jackman et al. [1986]*), it

is appropriate to fix the O_3 to measurements in all our model computations.

The H_2O was taken from the LIMS data (discussed by *Russell et al. [1984a]*) above about 100 mbar and elsewhere from two-dimensional model runs of *Guthrie et al. [1984b]*. The two distributions of H_2O meshed well with each other. Extrapolation to latitudes south of -65° was accomplished by using northern hemisphere data during a comparable season. H_2O produces HO_x (H , OH , and HO_2) by



and affects NO_2 and HNO_3 through the reactions



These reactions are important mainly in the stratosphere; thus the distribution of H_2O given by the LIMS data is much more important than the tropospheric model H_2O in determining the distribution of NO_2 and HNO_3 . We use the mean of the ascending/descending node results for each latitude [*Remsberg et al., 1984*]. There is an apparent diurnal variation in H_2O which starts to become significant between 2 and 1 mbar. This effect is not considered to be real by the principal investigators of the LIMS instrument [*Remsberg et al., 1984*], and since the H_2O is thought to be nearly constant between 2 mbar and 0.23 mbar (top of our two-dimensional model), we fix H_2O at 1.68 mbar and above to the LIMS measurements at 1.68 mbar. Since the LIMS H_2O measurements extended only through seven months, we needed to extrapolate for the other five months. This was done by assuming that the distribution of H_2O for the southern hemisphere summer was the same as that of northern hemisphere summer and that the distribution of H_2O for the northern hemisphere winter was the same as that of southern hemisphere winter. Since the data are relatively symmetric about the equator [see *Remsberg et al., 1984*], this assumption is probably a fairly good one.

The CH_4 and N_2O were both taken from SAMS data (discussed by *Jones and Pyle [1984]*, and *Jones [1984]*) when possible. These data were combined with two-dimensional model results of *Guthrie et al. [1984b]*. In general, the data and model results matched fairly well. We show the fixed N_2O in Figures 1a and 1b for March and December, respectively.

The densities of the species CFCl_3 and CF_2Cl_2 were taken from the paper of *Guthrie et al. [1984a]* for the year 1980 but were multiplied by a factor of 4 to obtain approximately 3 parts per billion by volume (ppbv) Cl_x in the stratosphere (an amount measured by *Berg et al. [1980]*). Our modeled ClO is in fair agreement with that measured by *Menzies [1979]*, *Anderson et al. [1980]*, *Weinstock et al. [1981]*, and *Brune et al. [1985]*. The $[\text{ClO}]$ in this study is similar to the $[\text{ClO}]$ shown in Figure 1 of *Jackman et al. [1986]*.

The major species N_2 (78% of the atmosphere), O_2 (21% of the atmosphere), and CO_2 (0.033% of the atmosphere) were computed using the temperature field from National Meteorological Center (NMC) and CIRA data and solving the hydrostatic equation. SAMS temperature data (discussed by *Rodgers et al. [1984]*), where available, were used for computation of the temperature-dependent reaction rates. Where SAMS temperature data were not available, the NMC and CIRA temperature data were used.

TABLE 1. Reactions and Their Rates

Number	Reaction	Rate Coefficient
(R1)	$O_2 + h\nu \rightarrow O + O$	$J_1 < 242 \text{ nm}$
(R2)	$O_3 + h\nu \rightarrow O_2 + O(^1D)^a$	$J_2 < 310 \text{ nm}$
(R3)	$O_3 + h\nu \rightarrow O_2 + O$	$J_3 < 1140 \text{ nm}$
(R4)	$NO + h\nu \rightarrow N + O$	$J_4 < 191 \text{ nm}$
(R5)	$NO_2 + h\nu \rightarrow NO + O$	$J_5 < 400 \text{ nm}$
(R6)	$NO_3 + h\nu \rightarrow NO + O_2$	$J_6 < 700 \text{ nm}$
(R7)	$NO_3 + h\nu \rightarrow NO_2 + O$	$J_7 < 700 \text{ nm}$
(R8)	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	$J_8 < 380 \text{ nm}$
(R9)	$N_2O + h\nu \rightarrow N_2 + O(^1D)$	$J_9 < 240 \text{ nm}$
(R10)	$H_2O + h\nu \rightarrow OH + H$	$J_{10} < 190 \text{ nm}$
(R11)	$HNO_3 + h\nu \rightarrow OH + NO_2$	$J_{11} < 546 \text{ nm}$
(R12)	$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$	$J_{12} < 330 \text{ nm}$
(R13)	$HO_2NO_2 + h\nu \rightarrow OH + NO_3$	$J_{13} < 330 \text{ nm}$
(R14)	$CFCl_3 + h\nu \rightarrow 3Cl$ + fragment ^b	$J_{14} < 260 \text{ nm}$
(R15)	$CF_2Cl_2 + h\nu \rightarrow 2Cl$ + fragment ^b	$J_{15} < 240 \text{ nm}$
(R16)	$HCl + h\nu \rightarrow Cl + H$	$J_{16} < 220 \text{ nm}$
(R17)	$HOCl + h\nu \rightarrow Cl + OH$	$J_{17} < 420 \text{ nm}$
(R18)	$ClO + h\nu \rightarrow Cl + O$	$J_{18} < 310 \text{ nm}$
(R19)	$ClONO_2 + h\nu \rightarrow Cl + NO_3$	$J_{19} < 450 \text{ nm}$
(R20)	$O + O_3 \rightarrow O_2 + O_2$	$k_{20} = 8.0(-12) \exp(-2060/T)^f$
(R21)	$O + O_2 + M \rightarrow O_3 + M$	k_{21} (see JPL 85-37)
(R22)	$O(^1D) + O_2 \rightarrow O + O_2$	$k_{22} = 3.2(-11) \exp(67/T)$
(R23)	$O(^1D) + N_2 \rightarrow O + N_2$	$k_{23} = 1.8(-11) \exp(107/T)$
(R24)	$O(^1D) + H_2O \rightarrow OH + OH$	$k_{24} = 2.2(-10)$
(R25)	$O(^1D) + N_2O \rightarrow N_2 + O_2$	$k_{25} = 4.9(-11)$
(R26)	$O(^1D) + N_2O \rightarrow NO + NO$	$k_{26} = 6.7(-11)$
(R27)	$NO + O_3 \rightarrow NO_2 + O_2$	$k_{27} = 1.8(-12) \exp(-1370/T)$
(R28)	$NO_2 + O \rightarrow NO + O_2$	$k_{28} = 9.3(-12)$
(R29)	$N + NO \rightarrow N_2 + O$	$k_{29} = 3.4(-11)$
(R30)	$N + O_2 \rightarrow NO + O$	$k_{30} = 4.4(-12) \exp(-3220/T)$
(R31)	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$k_{31} = 1.2(-13) \exp(-2450/T)$
(R32)	$NO_3 + NO \rightarrow NO_2 + NO_2$	$k_{32} = 1.3(-11) \exp(250/T)$
(R33)	$NO_3 + O \rightarrow NO_2 + O_2$	$k_{33} = 1.0(-11)$
(R34)	$NO + O + M \rightarrow NO_2 + M$	k_{34} (see JPL 85-37)
(R35)	$NO_2 + O + M \rightarrow NO_3 + M$	k_{35} (see JPL 85-37)
(R36)	$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$	k_{36} (see JPL 85-37)
(R37)	$N_2O_5 + H_2O \rightarrow HNO_3$ + HNO_3	$k_{37} = 2.0(-21)$
(R38)	$N_2O_5 + M \rightarrow NO_2$ + $NO_3 + M$	k_{38} (see JPL 85-37)
(R39)	$OH + O \rightarrow H + O_2$	$k_{39} = 2.2(-11) \exp(117/T)$
(R40)	$HO_2 + O \rightarrow OH + O_2$	$k_{40} = 3.0(-11) \exp(200/T)$
(R41)	$OH + O_3 \rightarrow HO_2 + O_2$	$k_{41} = 1.6(-12) \exp(-940/T)$
(R42)	$HO_2 + O_3 \rightarrow OH + O_2 + O_2$	$k_{42} = 1.4(-14) \exp(-580/T)$
(R43)	$H + O_3 \rightarrow OH + O_2$	$k_{43} = 1.4(-10) \exp(-470/T)$
(R44)	$H + O_2 + M \rightarrow HO_2 + M$	k_{44} (see JPL 85-37)
(R45)	$OH + HO_2 \rightarrow H_2O + O_2$	k_{45} (see JPL 85-37)
(R46)	$OH + OH \rightarrow H_2O + O$	$k_{46} = 4.2(-12) \exp(-242/T)$
(R47)	$H + HO_2 \rightarrow OH + OH$	$k_{47} = 6.4(-11)$
(R48)	$H + HO_2 \rightarrow H_2O + O$	$k_{48} = 3.0(-12)$
(R49)	$H + HO_2 \rightarrow H_2 + O_2$	$k_{49} = 6.7(-12)$
(R50)	$NO + HO_2 \rightarrow NO_2 + OH$	$k_{50} = 3.7(-12) \exp(240/T)$
(R51)	$OH + HNO_3 \rightarrow H_2O + NO_3$	k_{51} (see JPL 85-37)
(R52)	$OH + HO_2NO_2 \rightarrow H_2O$ + $O_2 + NO_2$	$k_{52} = 1.3(-12) \exp(380/T)$
(R53)	$O + HO_2NO_2 \rightarrow OH$ + $O_2 + NO_2$	$k_{53} = 7.0(-11) \exp(-3370/T)$
(R54)	$OH + NO_2 + M \rightarrow HNO_3 + M$	k_{54} (see JPL 85-37)
(R55)	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	k_{55} (see JPL 85-37)
(R56)	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	k_{56} (see JPL 85-37)
(R57)	$H_2 + O(^1D) \rightarrow H + OH$	$k_{57} = 1.0(-10)$
(R58)	$H_2 + OH \rightarrow H + H_2O$	$k_{58} = 6.1(-12) \exp(-2030/T)$
(R59)	$Cl + O_3 \rightarrow ClO + O_2$	$k_{59} = 2.8(-11) \exp(-257/T)$
(R60)	$ClO + O \rightarrow Cl + O_2$	$k_{60} = 4.7(-11) \exp(-50/T)$
(R61)	$HCl + OH \rightarrow Cl + H_2O$	$k_{61} = 2.6(-12) \exp(-350/T)$
(R62)	$Cl + CH_4 \rightarrow OH + HCl$ + fragment ^b	$k_{62} = 9.6(-12) \exp(-1350/T)$
(R63)	$Cl + H_2 \rightarrow HCl + H$	$k_{63} = 3.7(-11) \exp(-2300/T)$
(R64)	$Cl + HO_2 \rightarrow HCl + O_2$	$k_{64} = 1.8(-11) \exp(170/T)$
(R65)	$Cl + HO_2 \rightarrow OH + ClO$	$k_{65} = 4.1(-11) \exp(-450/T)$

TABLE 1. (continued)

Number	Reaction	Rate Coefficient
(R66)	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$k_{66} = 4.6(-13) \exp(710/T)$
(R67)	$\text{HOCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{ClO}$	$k_{67} = 3.0(-12) \exp(-150/T)$
(R68)	$\text{ClONO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_3$	$k_{68} = 1.2(-12) \exp(-333/T)$
(R69)	$\text{ClONO}_2 + \text{O} \rightarrow \text{ClO} + \text{NO}_3$	$k_{69} = 3.0(-12) \exp(-808/T)$
(R70)	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$k_{70} = 6.2(-12) \exp(294/T)$
(R71)	$\text{CFCl}_3 + \text{O}(^1D) \rightarrow 2\text{Cl}$ + ClO + fragment ^b	$k_{71} = 2.3(-10)$
(R72)	$\text{CF}_2\text{Cl}_2 + \text{O}(^1D) \rightarrow \text{Cl}$ + ClO + fragment ^b	$k_{72} = 1.4(-10)$
(R73)	$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow$ $\text{ClONO}_2 + \text{M}$	k_{73} (see JPL 85-37)

Rates correspond to those recommended by DeMore *et al.* [1985] (herein designated as JPL 85-37). Units for photolysis processes are s^{-1} , binary reactions are $\text{cm}^3 \text{s}^{-1}$, and tertiary reactions are $\text{cm}^6 \text{s}^{-1}$.

^aSpin conservation is not violated. $\text{O}_2(^1\Delta)$ is assumed to quench to O_2 rapidly.

^bProducts in these reactions, (R14), (R15), (R62), (R71), and (R72), are best guesses which help to speed up convergence of our two-dimensional model. Thus the right-hand side of the reaction may not necessarily balance the left-hand side.

^c $8.0(-12)$ means 8.0×10^{-12} .

COMPUTATION OF NO_2 AND HNO_3 AND COMPARISON TO LIMS DATA

We used the two-dimensional model of Guthrie *et al.* [1984a, b] with certain species fixed as described in the last section. For the base case model computation we used the diabatic circulation as computed from the use of heating rates given by Rosenfeld *et al.* [1987]. We have included the effects of scattering of photons in all calculations utilizing the two-stream radiative transfer method discussed by Herman [1979], which is based on the matrix operator method of Plass *et al.* [1973]. The reactions and their rate coefficients used in our model computations are given in Table 1.

We ran the model for a simulated time of three years at which time a repeating pattern was observed in the NO_2 and HNO_3 distributions. The distributions of NO_2 and HNO_3 were then compared to LIMS data for the months of March and December. LIMS NO_2 and HNO_3 were discussed extensively in the validation papers by Russell *et al.* [1984b] and Gille *et al.* [1984], respectively. We discuss the uncertainties in our calculation and sensitivity studies to help in understanding the computations in the following sections.

We have compared our odd nitrogen (also referred to as NO_x in this paper) production rates with those of Crutzen and Schmailzl [1983] and some earlier studies. Our computed global diurnal average NO_x production rate is about $1.7 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$, in fairly good agreement with the Crutzen and Schmailzl [1983] calculation of $1.5 \pm 0.4 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$. We disagree with the values computed by Jackman *et al.* [1980] and by Johnston *et al.* [1979], which showed NO_x production rates of about $2.9 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$. There are several differences between this study and the Jackman *et al.* [1980] study, including the N_2O distributions, O_3 distributions, solar flux values, and a 15% error in the work by Jackman *et al.* [1980] for the production of $\text{O}(^1D)$ from photolysis of O_3 . However, the largest difference between the two calculations is the difference in the N_2O distributions. The N_2O values used by Jackman *et al.* [1980] in the middle stratosphere are about a factor of 1.7 larger than those used in this paper, a factor which is approximately equal to the ratio of the NO_x production from Jackman *et al.* [1980] and the NO_x production rate computed in this work.

We can calculate either the daytime or nighttime concentrations of NO_2 and HNO_3 from our diurnal average concentrations. The method of Turco and Whitten [1978] was used in deriving the diurnal average concentrations. We invert the diurnal average computation and use the night to day ratios obtained from the one-dimensional model of Herman and McQuillan [1985] as well as the fraction of day and night at each grid point in the model to derive the daytime or nighttime concentrations.

The nighttime LIMS NO_2 data for March and December are presented in Figures 2a and 2b, respectively. We compare with the nighttime data, as these data appear to be more reliable [see Callis *et al.*, 1985, 1986], at least for NO_2 . The nighttime NO_2 data are more reliable because of the larger signal/noise ratio which is a consequence of generally higher levels of NO_2 at night. Note that our model-computed nighttime NO_2 values are slightly less than those given by Callis *et al.* [1985] at the peak of NO_2 . We are working with the profile archived data (which have been obtained from the National Space Sciences Data Center at the Goddard Space Flight Center) while Callis *et al.* [1985] use a radiance average to derive their NO_2 distribution (radiance average method was first described by Russell *et al.* [1984c]). The computed nighttime NO_2 for March and December is presented in Figures 3a and 3b, respectively. An effective way to compare two sets of results is to plot their ratio. We thus take the ratios of the computed NO_2 to the LIMS NO_2 and present these ratios in Figures 4a and 4b for March and December.

The model and LIMS NO_2 are in relatively good agreement in the upper stratosphere, at least for March. Since this is the region where nighttime NO_2 is close to the total amount of NO_x [Callis *et al.*, 1985], we can conclude that the model total NO_x is, within the uncertainties of the calculation (see section on uncertainties), approximately equal to the atmospheric NO_x in the upper stratosphere. This result, however, might be fortuitous in view of the differences detailed below. We should also note that there is a substantial day to night change in NO_2 in the upper stratosphere. Thus the model nighttime NO_2 should not necessarily agree with the LIMS nighttime NO_2 because the LIMS nighttime NO_2 is taken at a specific local time (which changes rapidly with latitude near the poles)

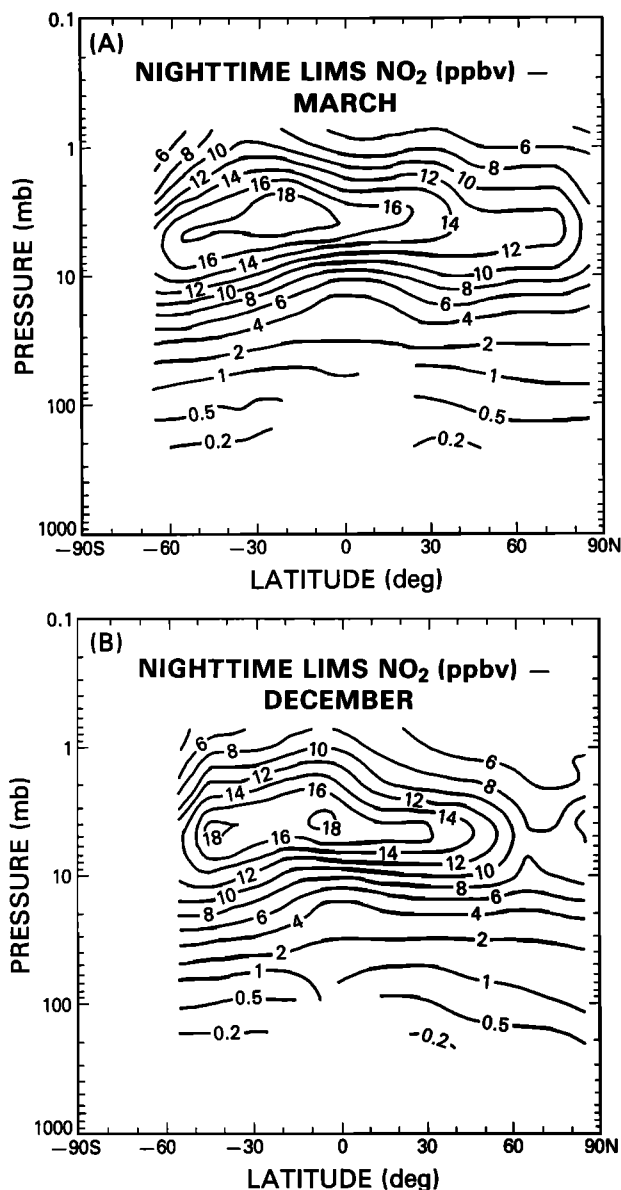


Fig. 2. LIMS nighttime NO_2 for (a) March and (b) December.

and the model nighttime NO_2 is a nighttime averaged quantity.

There are several differences that stand out in Figure 4. A large discrepancy between the computed and the measured NO_2 distribution occurs in the lower part of the stratosphere and at the lowest latitudes, where ratios reach a factor of four and more. These differences should be considered when taken in the context that LIMS NO_2 uncertainties are largest at 50 mbar and below, reaching values of 84% [Russell *et al.*, 1984b]. Notwithstanding these large uncertainties in LIMS data, it is clear that the computed NO_2 is much less than the measured NO_2 in the lower stratosphere. Nicolet [1975b] has suggested that galactic cosmic rays can be a source of NO_x in the lower stratosphere, especially at the high latitudes, and Noxon [1976], Tuck [1976], Chameides *et al.* [1977], Logan [1983], and Borucki and Chameides [1984] have speculated on a source of NO_x through lightning which Ko *et al.* [1986] noted could produce more NO_2 in the lower stratosphere at the low latitudes. We investigate the influence of these sources in the section on sensitivity studies.

Another difference which stands out is the fact that the computed NO_2 is over a factor of 2 larger than the measured NO_2 in the upper stratosphere above 3 mbar in the northern latitudes during December. Our model shows an asymmetry in NO_2 with a bias toward the winter hemisphere. The LIMS data show an asymmetry with a bias, which is still being discussed [Callis *et al.*, 1985, 1986], toward the southern hemisphere during most of the LIMS observing time frame.

Three possible explanations for the LIMS southern hemisphere bias were given by Callis *et al.* [1986]. The first is that the satellite observing time for measuring NO_2 biases it toward larger values in the southern hemisphere than the northern hemisphere. The second contribution to the asymmetry might be the cooler temperatures at latitudes poleward of 30° in the northern hemisphere when compared with the southern hemisphere, at least for March. The third possibility was that the N_2O shows a similar bias which would therefore be reflected in the NO_2 measurements. Callis *et al.* [1986] question this third possibility due to the long characteristic

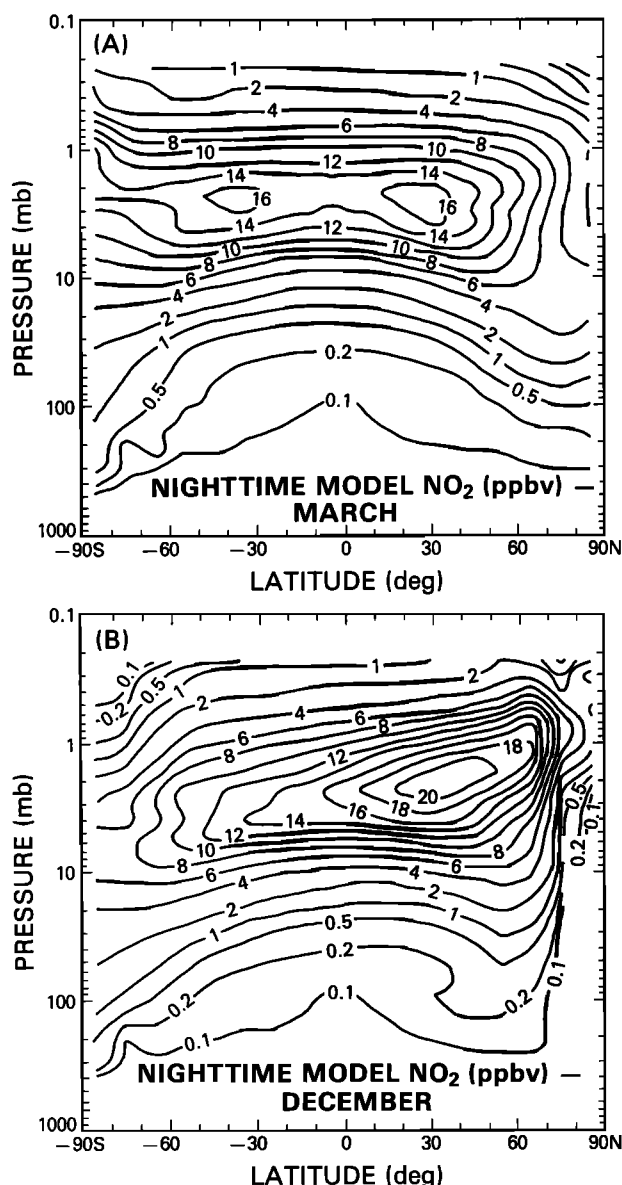


Fig. 3. Model-computed NO_2 for (a) March and (b) December in the base run.

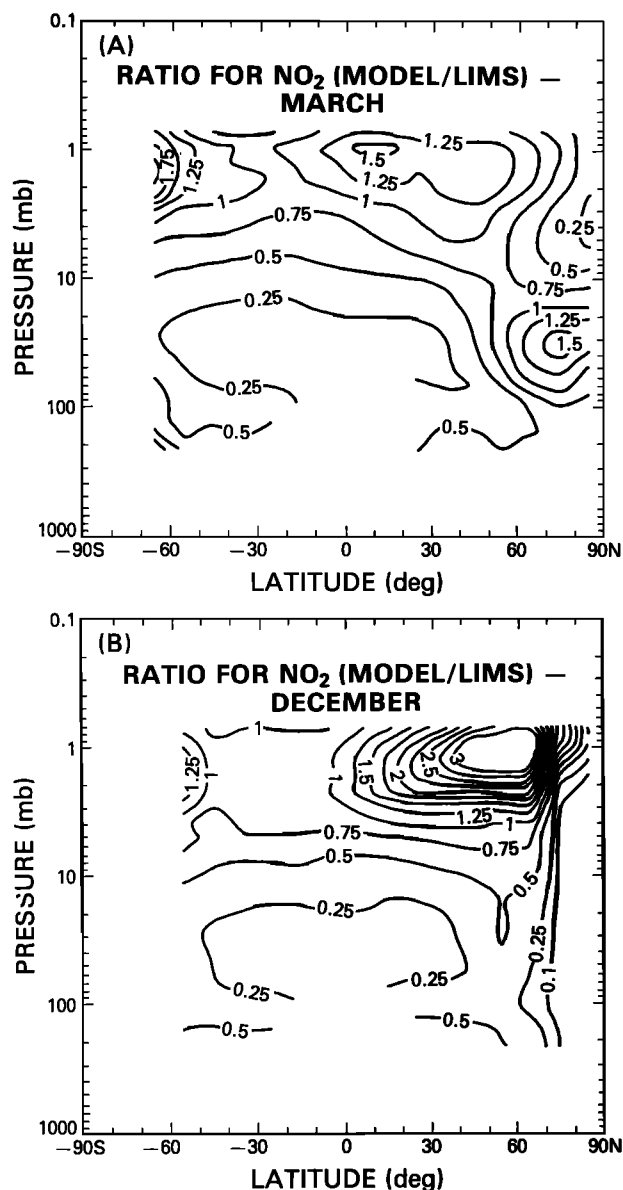


Fig. 4. Ratio of model-computed NO_2 to LIMS NO_2 for (a) March and (b) December.

time required for odd nitrogen production due to the $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ reaction (in excess of 200 days at 40 km).

We have observed from our computations that this third possibility explaining the NO_2 measurements cannot be correct as our derived NO_2 show a bias toward the northern hemisphere during most of the time period for the LIMS measurements (mainly the northern hemisphere fall and winter). Indications from comparing our model and LIMS data are that the circulation transports NO_x to the upper stratosphere at high latitudes during the summer and fall. This combined with the tendency for NO_x to be in the form of NO_2 at large solar zenith angles [see Solomon *et al.*, 1986b, Figures 2 and 3] leads to an overabundance of NO_2 in this region at the winter solstice when compared to the LIMS data. This result is in agreement with a study by Schmailzl and Crutzen [1985] which showed a distinct overestimation in calculated NO_2 (as well as HNO_3 and possibly NO) when compared with balloon measurements at altitudes above 30 km.

There have been several sources of NO_x postulated for these upper levels of the stratosphere, including a downflux from the thermosphere, solar proton events, and relativistic electron precipitation events [see Jackman *et al.*, 1980, and references therein]. Large fluctuations in NO_2 in the upper stratosphere and mesosphere have in fact been measured by Russell *et al.* [1984c]. These measurements indicate a buildup of mesospheric and stratospheric NO_2 during the polar night. Since our model results show more NO_2 in the winter middle latitudes than the measurements, the inclusion of this source in our calculations would only make the disagreement even worse. As pointed out by Russell *et al.* [1984c], this is mainly a high-latitude upper stratospheric and mesospheric source of NO_x . There were not any significant solar proton events (that might have affected the stratosphere) during the LIMS observing period (Solar Geophysical Data, 1979–1980). The precipitation by relativistic electrons affects the mesosphere more than the stratosphere [see Jackman *et al.*, 1980] and probably is not important as a NO_x source for the stratosphere during the LIMS observing period.

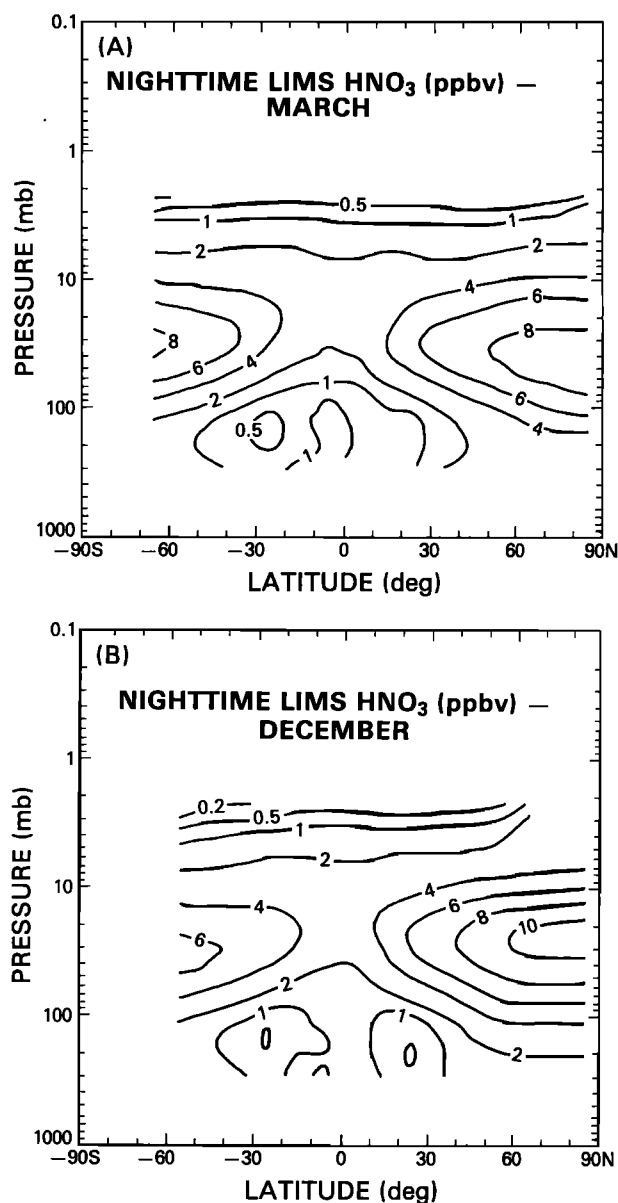


Fig. 5. LIMS nighttime HNO_3 for (a) March and (b) December.

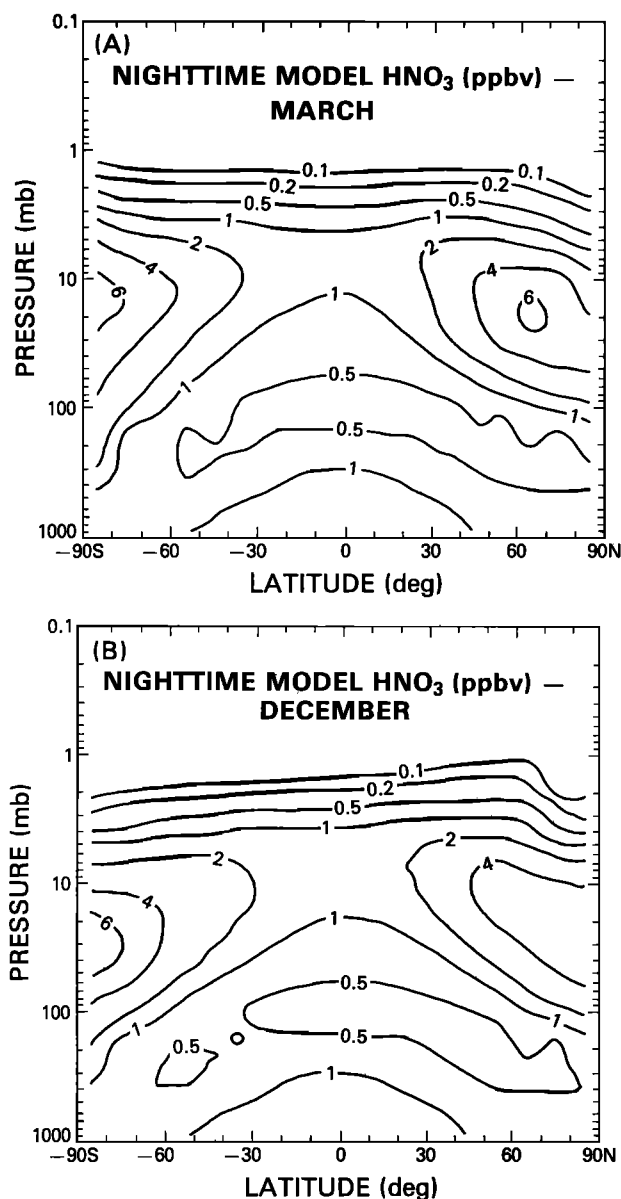


Fig. 6. Model-computed HNO_3 for (a) March and (b) December in the base run.

Solomon *et al.* [1986b] have presented model calculations that are able to reproduce the LIMS NO_2 observations quite well at a variety of solar zenith angles, altitudes, and latitudes. Our work complements the Solomon *et al.* [1986b] study since their results reflect the diurnal variation of NO_2 , whereas ours was concerned with the seasonal changes and zonally averaged distribution of NO_2 . The Solomon *et al.* [1986b] findings are not necessarily contrary to those of this study, as their study was constrained to reproduce the NO_x observed by the LIMS measurements. We do not have a similar constraint on NO_x in our model computations; however, we do have other constraints on our calculations which have been pointed out previously.

How does calculated HNO_3 compare with LIMS HNO_3 ? We first plot the LIMS nighttime measurements in Figures 5a and 5b for March and December, respectively. In Figure 6 we plot the computed values of HNO_3 for March and December. The peak of HNO_3 occurs at a slightly higher altitude in the computations (this difference has been observed before in

other one-dimensional and two-dimensional computations; see pp. 1–178 from the *World Meteorological Organization* [1982]) and a lower mixing ratio than in the measurements. Also, the HNO_3 is larger in the summer hemisphere than in the winter hemisphere for the computations, and just the opposite is true for the measurements. We present the ratio of the measurements to the computations in Figure 7. The HNO_3 from both the measurements and the computations are in relative agreement in the upper stratosphere and lower-latitude region. Note that the LIMS HNO_3 has been modified above 5 mbar by the scheme given by Jackman *et al.* [1985].

It is a fairly reasonable assumption that total NO_x in the upper stratosphere is the sum of nighttime NO_2 and HNO_3 . For most latitudes and altitudes, nighttime $\text{NO}_2 + \text{HNO}_3$ represents more than 75% of NO_x (from Callis *et al.* [1985] and also our own computations). A comparison of computed nighttime $\text{NO}_2 + \text{HNO}_3$ with LIMS nighttime $\text{NO}_2 + \text{HNO}_3$ is shown in Figure 8 for December. The computed NO_2

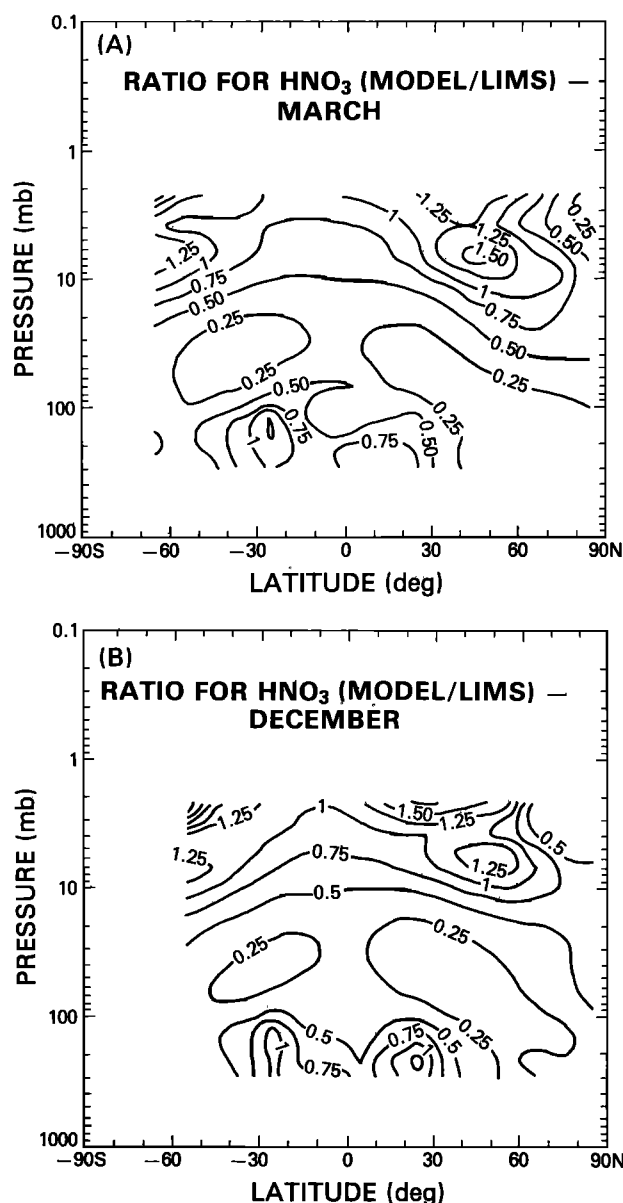


Fig. 7. Ratio of model-computed HNO_3 to LIMS HNO_3 for (a) March and (b) December.

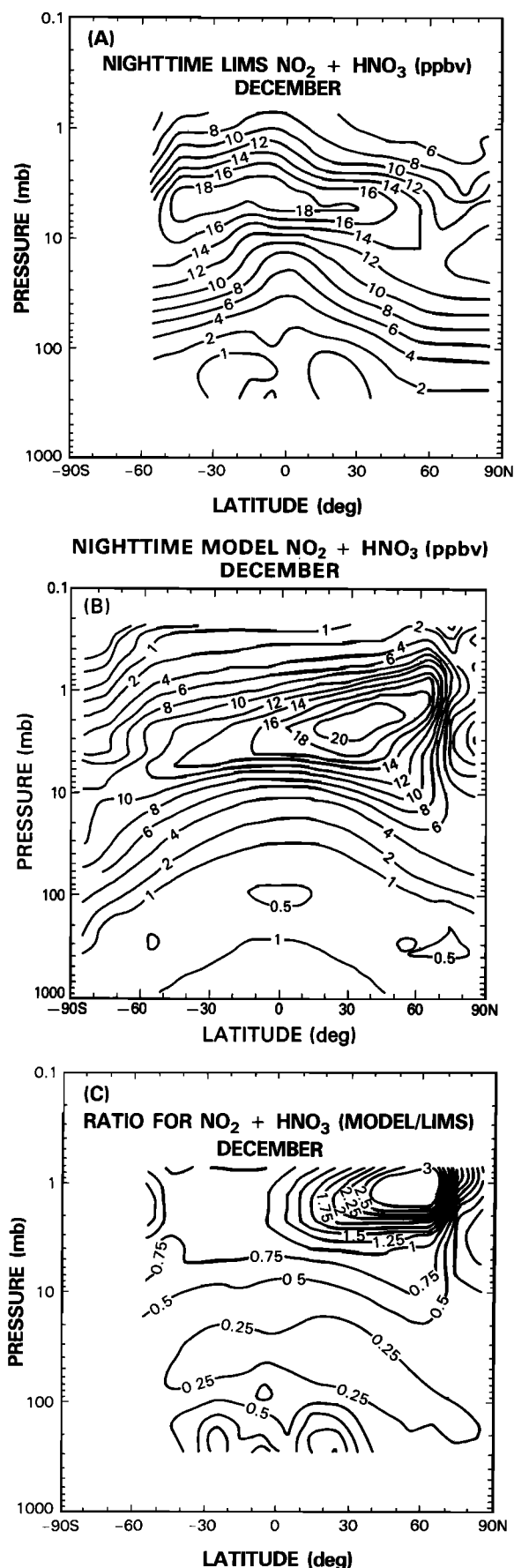


Fig. 8. (a) LIMS nighttime $\text{NO}_2 + \text{HNO}_3$, (b) model-computed $\text{NO}_2 + \text{HNO}_3$, and (c) ratio of model-computed $\text{NO}_2 + \text{HNO}_3$ to LIMS $\text{NO}_2 + \text{HNO}_3$ all for the month of December.

+ HNO_3 is over a factor of 2 larger than the LIMS $\text{NO}_2 + \text{HNO}_3$ in the upper stratosphere above 3 mbar in the northern latitudes. This finding indicates that HNO_3 is not the reservoir for the difference between derived and LIMS NO_2 discussed earlier. We have also examined nighttime $\text{NO}_2 + \text{HNO}_3$ during March. We find fairly good agreement in the upper stratosphere, similar to our result from comparing model to LIMS NO_2 .

UNCERTAINTY CALCULATION

We have noted some differences between the model computations and the measurements in the last section. Just what are the uncertainties in the computations? This is a very difficult question to answer because the dynamics of the stratosphere are extremely important in determining the NO_2 and HNO_3 distributions. Uncertainties in the dynamics are difficult to compute. Because of transport, the uncertainties at a single grid point in a model can be transposed to neighboring grid points quite rapidly. At the present time we are not able to keep track of the movement of these dynamical uncertainties and their propagation throughout the model. However, we are able to compute uncertainties at single grid points where photochemical equilibrium is a reasonable approximation, say above about 2 mbar at the low latitudes, using the method described by Kaye and Jackman [1986a, b]. See discussion below for an indication of how reasonable this photochemical equilibrium assumption is.

An analytic expression for the NO_2 computation can be calculated using the following reasoning: The production of NO_x , $P(\text{NO}_x)$, is given by

$$P(\text{NO}_x) = 2k_{26}[\text{N}_2\text{O}][\text{O}(^1D)] \quad (1)$$

(shown in Figure 9a), and the major loss of NO_x in the upper stratosphere (u.s.) is given by

$$L(\text{NO}_x)_{\text{u.s.}} = 2k_{29}[\text{N}][\text{NO}] \quad (2)$$

(shown in Figure 9b). In the troposphere (t.) and lower stratosphere (l.s.) the loss of NO_x is

$$L(\text{NO}_x)_{\text{t.,l.s.}} = \text{rainout of } \text{HNO}_3 \quad (3)$$

(shown in Figure 9c). The total loss of NO_x , $L(\text{NO}_x)_T$, then is

$$L(\text{NO}_x)_T = L(\text{NO}_x)_{\text{u.s.}} + L(\text{NO}_x)_{\text{t.,l.s.}} \quad (4)$$

and the ratio $L(\text{NO}_x)_T/P(\text{NO}_x)$ is shown in Figure 9d.

It should be noticed that $P(\text{NO}_x) = L(\text{NO}_x)_{\text{u.s.}}$ (i.e., the ratio of $L(\text{NO}_x)_T/P(\text{NO}_x)$ is 1.0) between about 1 and 2 mbar at low latitudes. At this level,

$$[\text{NO}] = \frac{k_{26}[\text{N}_2\text{O}][\text{O}(^1D)]}{k_{29}[\text{N}]} \quad (5)$$

For NO_2 we have

$$P(\text{NO}_2) = k_{27}[\text{NO}][\text{O}_3] + k_{70}[\text{ClO}][\text{NO}] \quad (6)$$

$$L(\text{NO}_2) = k_{28}[\text{NO}_2][\text{O}] + J_5[\text{NO}_2] \quad (7)$$

Since $P(\text{NO}_2) = L(\text{NO}_2)$,

$$[\text{NO}_2] = \frac{[\text{NO}](k_{27}[\text{O}_3] + k_{70}[\text{ClO}])}{k_{28}[\text{O}] + J_5} \quad (8)$$

The production rate for $\text{O}(^1D)$ is given by

$$P(\text{O}(^1D)) = J_2[\text{O}_3] \quad (9)$$

$$L(\text{O}(^1D)) = k_{23}[\text{O}(^1D)][\text{N}_2] + k_{22}[\text{O}(^1D)][\text{O}_2] \quad (10)$$

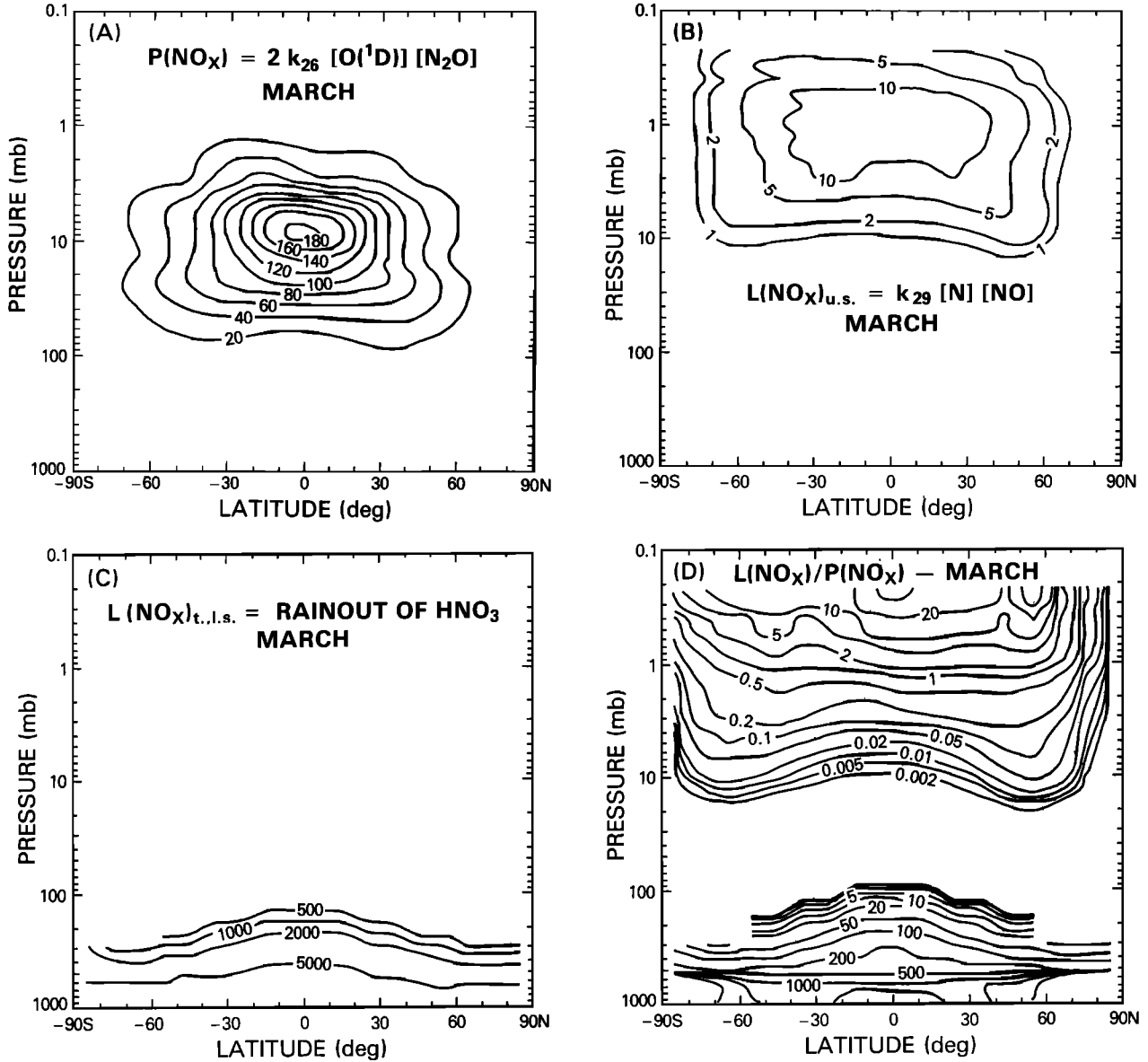


Fig. 9. (a) Odd nitrogen production due to reaction of $O(^1D)$ with N_2O to produce $NO + NO$, (b) odd nitrogen loss due to reaction of N with NO to produce N_2 and O , (c) odd nitrogen loss due to rain-out of HNO_3 , and (d) ratio of odd nitrogen loss to production. Units in Figures 9a–9c are $cm^{-3} s^{-1}$.

and if we assume that $O(^1D)$ is in photochemical equilibrium throughout the stratosphere, then we obtain

$$[O(^1D)] = \frac{J_2[O_3]}{k_{23}[N_2] + k_{22}[O_2]} \quad (11)$$

We also know that in the stratosphere,

$$P(O) = (J_2 + J_3)[O_3] \quad (12)$$

$$L(O) = k_{21}[O][O_2][M] \quad (13)$$

and if we assume that atomic oxygen is in photochemical equilibrium throughout the stratosphere, then

$$[O] = \frac{(J_2 + J_3)[O_3]}{k_{21}[O_2][M]} \quad (14)$$

Substituting (5), (11), and (14) into (8), we get an expression

useful between about 1 and 2 mbar at low latitudes,

$$\begin{aligned} [NO_2] = & \{k_{26}[N_2O]J_2[O_3](k_{27}[O_3] \\ & + k_{70}[ClO])k_{21}[O_2][M]\} \\ & \cdot \{k_{29}[N](k_{23}[N_2] + k_{22}[O_2]) \\ & \cdot (k_{28}\{J_2 + J_3\}[O_3] + J_5k_{21}[O_2][M])\}^{-1} \end{aligned} \quad (15)$$

We used (15) to compute NO_2 and compared it with the value from the model for NO_2 . We find that analytic formula (15) underestimates NO_2 by about 20%. This is not surprising because the circulation should transport NO_x from lower altitudes to this region and, also, the lifetime for NO_x in this region is of the order of months, i.e., the assumption of photochemical equilibrium is not true. Since dynamics is causing an error in $[NO_2]$ only of the order of 20%, we feel justified to

TABLE 2. Major Terms Involved in Uncertainty Calculations of NO₂ Between 2 and 1 mbar Near the Equator

$S_{\text{NO}_2,j}$	Value of $S_{\text{NO}_2,j}$	f_j	$(S_{\text{NO}_2,j} \ln f_j)^2$
$S_{\text{NO}_2,\text{N}}$	-1	see text	see text
$S_{\text{NO}_2,\text{N}_2\text{O}}$	1	1.5	1.64(-1)
$S_{\text{NO}_2,k_{26}}$	1	1.3	6.86(-2)
$S_{\text{NO}_2,k_{29}}$	-1	1.3	6.86(-2)
S_{NO_2,J_2}	0.501	1.4	2.83(-2)
$S_{\text{NO}_2,k_{27}}$	0.891	1.2	2.63(-2)
$S_{\text{NO}_2,k_{23}}$	-0.714	1.2	1.69(-2)
$S_{\text{NO}_2,k_{21}}$	0.661	1.16	9.57(-3)
S_{NO_2,J_5}	-0.339	1.3	7.89(-3)
$S_{\text{NO}_2,k_{28}}$	-0.661	1.1	3.97(-3)
$S_{\text{NO}_2,k_{22}}$	-0.288	1.2	2.75(-3)
S_{NO_2,J_3}	-0.163	1.1	2.41(-4)
$S_{\text{NO}_2,k_{70}}$	0.109	1.15	2.33(-4)
$S_{\text{NO}_2,\text{O}_3}$	0.364	1.04	2.02(-4)
$S_{\text{NO}_2,\text{ClO}}$	0.109	see text	see text

Read 1.64(-1) as 1.64×10^{-1} .

go on with an uncertainty computation which is based on the photochemical equilibrium assumption. We perform this analysis primarily to have a first-order indication of the accuracy of our computations and, also, to highlight those parameters to which NO₂ is most sensitive.

We use the procedure detailed by *Kaye and Jackman* [1986a, b] to compute the uncertainty in the NO₂ computation. This method yields multiplicative values for uncertainties u_i in the inferred concentrations of trace species i ; that is, a species found to have concentration $[M_i]$ with uncertainty u_i is expected to lie in the range from $[M_i]/u_i$ to $u_i[M_i]$. Uncertainties are calculated by the expressions

$$u_i = \exp[\sum_j (S_{ij} \ln f_j)^2]^{1/2} \quad (16)$$

where S_{ij} is the sensitivity coefficient (logarithmic derivative)

$$S_{ij} = \partial \ln [M_i] / \partial \ln P_j = \frac{P_j}{[M_i]} \frac{\partial [M_i]}{\partial P_j} \quad (17)$$

and f_j is the uncertainty in parameter j .

In Table 2 we consider which of the model input parameters make the largest contributions to the computation of the uncertainty in NO₂ near the equator between 2 and 1 mbar (about 45 to 50 km). The uncertainties in the reaction rates and photodissociation rates are taken from *DeMore et al.* [1985] while the uncertainty in [N₂O] is taken from *Jones and Pyle* [1984] and the uncertainty in [O₃] is taken from *McPeters et al.* [1984].

The total uncertainty in the [NO₂] calculated using this procedure is about a factor of 1.9. This factor does not include the constituent uncertainties for [N] and [ClO]. The sensitivity coefficient for [ClO] is only 0.109; thus unless the uncertainty is quite large, such as a factor of 8 or more, the term $(S_{\text{NO}_2,\text{ClO}} \ln f_{\text{ClO}})^2$ is not going to add significantly to the total uncertainty. Knowledge of the uncertainty in the [N] calculation is quite crucial, however, because the sensitivity coefficient is -1. Since [N] is inversely related to [NO₂] (see equation (15)), we can assume that the uncertainty in [N] is related to the uncertainty in [NO₂]. For the purposes of this calculation we assume that the uncertainty in [N] is the same as that of [NO₂], a factor of 1.9. With this assumption we find that the uncertainty in [NO₂] jumps to 2.4. It is probably reasonable to conclude that the uncertainty in the [NO₂]

computation is between a factor of 2 and 3 from photochemistry alone. Our computations would be more uncertain if uncertainties in the dynamics were included as well. Analysis of the uncertainties in the dynamics and their effects on the total uncertainty in the calculation of [NO₂] is beyond the scope of this work.

Four terms in the uncertainty (shown in Table 2) account for about a factor of 1.8 themselves. These are the uncertainties in (1) the measurement of N₂O, (2) the reaction rate of O(¹D) with N₂O (leading to the production of NO_x), (3) the reaction rate of N with NO (leading to the destruction of NO_x), and (4) the photolysis of O₃ leading to O(¹D) production. Measurements of N₂O, k_{26} , k_{29} , and J_2 to greater accuracy are required in order to reduce the uncertainty of our calculations and give us an opportunity to improve our understanding of the NO_x photochemistry.

The measurements and computations of NO₂ are within their uncertainties of being in agreement in the upper stratosphere northern latitudes in December. However, there is an area of disagreement in the upper stratosphere at high latitudes (see Figure 4). We believe that this indicates that our understanding of the NO_x dynamics and/or photochemistry in this region is not complete. We discuss this subject more completely in the next section.

Computing the uncertainties in the calculation of NO₂ for areas lower in the stratosphere where dynamics is more dominant is extremely difficult. We did undertake a sensitivity study to determine the effect of a slightly different dynamics on our computed NO₂, which is discussed in the next section.

Before discussing several sensitivity studies we compute the uncertainty in the HNO₃, using an analysis similar to that used for NO₂. The uncertainty was found to be between a factor of 2.5 and 3 in the photochemical region in the upper

TABLE 3. Sensitivity Studies and Net Results When Compared With the Base Run

Sensitivity Study	Net Result
Weaker diabatic circulation used	Similar to result with base case circulation (see text)
Photochemical equilibrium everywhere—no transport	Indicates NO _x must be transported either upward or downward away from the low-latitude, middle stratosphere source region of N ₂ O + O(¹ D)
Run with computed N ₂ O	Indicates that transport must be present in the low-latitude and low and middle stratospheric region. Also, indicates that the N ₂ O source of NO _x is fairly well modeled and that low stratospheric low-latitude source of NO _x is missing
Use 2 ppbv of Cl _x	Similar to base result
Add galactic cosmic ray source of NO _x	Similar to base result
Use L4 lightning source of Ko <i>et al.</i> [1986]	Computed NO ₂ + HNO ₃ increased in lower stratosphere but LIMS NO ₂ + HNO ₃ still larger
Use H4 lightning source of Ko <i>et al.</i> [1986]	Computed NO ₂ + HNO ₃ increase even more than in preceding study in the lower stratosphere but LIMS NO ₂ + HNO ₃ still larger by a factor of 2
Increase N ₂ O ₅ + H ₂ O reaction rate by a factor of 100	Computed HNO ₃ peak now in winter like observations but still at too high an altitude

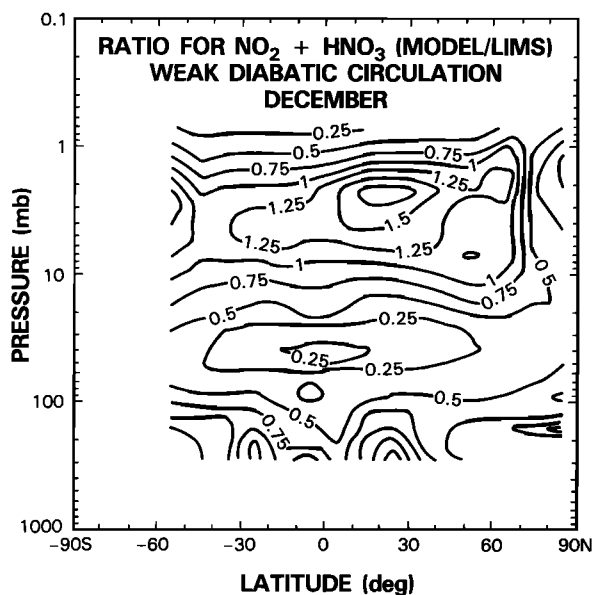


Fig. 10. Ratio of model-computed $\text{NO}_2 + \text{HNO}_3$ to LIMS $\text{NO}_2 + \text{HNO}_3$ for the month of December using the circulation discussed by Guthrie *et al.* [1984a].

stratosphere lower-latitude region. Near 10 mbar and above, the differences between the LIMS measurements and computations are well within the uncertainties of this calculation. Dynamics is certainly important in the distribution of HNO_3 at pressures greater than about 5 mbar (especially at the higher latitudes). As we noted earlier when discussing uncertainties in the calculation of NO_2 , it is quite difficult to compute uncertainties in the computation which includes dynamics. We do, however, discuss the problems noted between HNO_3 measurements and computations in the next section and offer a partial solution to the differences between the two.

SENSITIVITY STUDIES

We next discuss several sensitivity studies which indicate how robust our findings on NO_2 and HNO_3 are for the middle to lower stratospheric region. Because of the relatively large number of these studies, we have summarized our findings in Table 3.

We are using a dynamics which is dominated by the diabatic circulation, as explained by Guthrie *et al.* [1984a]. We use a diabatic circulation which is stronger than that given by Guthrie *et al.* [1984a] for our base case. This stronger circulation (larger vertical and meridional winds) has more basis in reality and is discussed by Rosenfield *et al.* [1987]. This stronger circulation is quite similar to the diabatic circulation derived by Solomon *et al.* [1986a] using LIMS data. We have also used the weaker diabatic circulation of Guthrie *et al.* [1984a] and find essentially the same results: (1) Calculated NO_2 is lower than the LIMS NO_2 in much of the lower stratosphere by about a factor of 4 or more; and (2) the derived HNO_3 at polar latitudes is highest in the summer while LIMS HNO_3 is highest in the winter.

We do find some differences, however, in using the weaker circulation. We find that the NO_x is not transported as effectively from its source region in the middle stratosphere to the higher altitudes, leading to larger peak values of NO_2 between 3 and 5 mbar and lower values of NO_2 above 3 mbar. The large differences in December in the high-latitude upper stratosphere are not as accentuated, but the model NO_2 in the

middle latitudes and middle to upper stratosphere is larger than LIMS NO_2 by up to a factor of 1.75. Note that this is precisely the region where the older circulation, based on an arbitrary scaling of the Murgatroyd and Singleton [1961] heating rates, is most likely to be incorrect. The model HNO_3 , however, shows an overabundance of up to a factor of 2 when compared with LIMS HNO_3 in the middle to high latitudes for the middle stratosphere. The ratio of nighttime $\text{NO}_2 + \text{HNO}_3$ from this weaker circulation to the LIMS nighttime $\text{NO}_2 + \text{HNO}_3$ is shown in Figure 10.

The only way (that we know of) to obtain relative agreement between the NO_2 observations and the NO_2 from our calculation in the lower stratosphere without adding any new NO_x source is to have a wind pattern which blows air essentially downward throughout the stratosphere in the low latitudes. Obviously, this would take NO_2 away at the top of the stratosphere and deposit more NO_2 in the lower stratosphere where it is needed. This circulation is contrary to the Brewer-Dobson circulation indicated in the LIMS H_2O data [see Remsberg *et al.*, 1984, and references therein].

We have done a sensitivity study which contained only photochemistry (i.e., the model was run with no transport). The results of this study are shown in Figure 11 where the ratio of the model nighttime $\text{NO}_2 + \text{HNO}_3$ to the LIMS nighttime $\text{NO}_2 + \text{HNO}_3$ is plotted. In this model computation the model nighttime $\text{NO}_2 + \text{HNO}_3$ was over a factor of 2 larger than the LIMS $\text{NO}_2 + \text{HNO}_3$ in the middle stratosphere at low latitudes but was a factor of 2 less than the LIMS $\text{NO}_2 + \text{HNO}_3$ in most of the lower stratosphere and in the upper stratosphere. This argues for a circulation that moves the NO_x away from the source region, either upward or downward.

We also have done a study similar to that described by Guthrie *et al.* [1984a] except only N_2O , $\text{O}(^1\text{D})$, and $\text{O}(^3\text{P})$ were computed with O_3 , O_2 , and N_2 held fixed. The resultant N_2O (see Figure 12) shows a structure similar to that observed in the SAMS data: A bubble is observed at low latitudes, representing the effect of upward flowing tropical air. Smaller mixing ratios are observed at higher latitudes for a given fixed

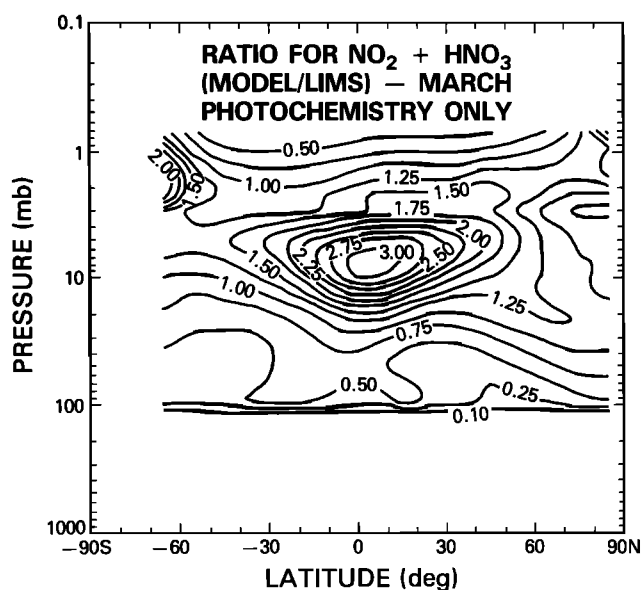


Fig. 11. Ratio of model-computed nighttime $\text{NO}_2 + \text{HNO}_3$ to LIMS nighttime $\text{NO}_2 + \text{HNO}_3$ for the month of March when model was run only with photochemistry and no dynamics.

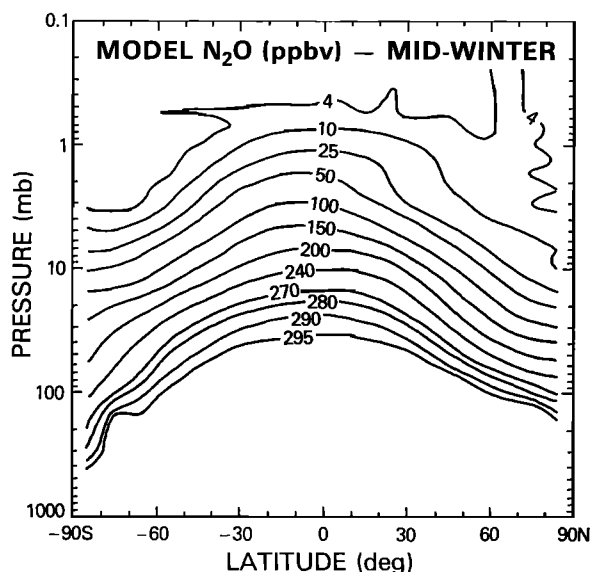


Fig. 12. N_2O distribution at day 36 (midwinter) of the year from model run with computed N_2O .

pressure level. The double-peaked behavior observed in the SAMS data in the upper stratosphere for certain months cannot be modeled correctly, but the overall structure is modeled fairly well. (As an aside we should note that *Gray and Pyle* [1986] have been fairly successful at modeling the double-peaked behavior observed in the SAMS data through forcing an equatorial semiannual oscillation by prescribing a suitable momentum convergence.) This leads us to the conclusion that the transport and diffusion in our model are not inconsistent with observed N_2O . Since the N_2O falls off at higher altitudes at approximately the same rate in both the model and SAMS data, this also is an indication that there is another source of NO_x in the lower stratosphere which is necessary to solve the problem of too small an amount of derived NO_2 and HNO_3 when compared with the LIMS NO_2 and HNO_3 .

We also find essentially the same results when we use an atmosphere in our model which has only 2 ppbv of Cl_x in the upper stratosphere as for one which has 3 ppbv of Cl_x . This means that other parameters are more important for the computation of NO_2 and HNO_3 than is the distribution and abundance of Cl_x .

We have included a NO_x source from galactic cosmic rays (GCRs) using the ion pair production rate as given by *Nicolet* [1975b] and assuming a NO_x production of 1.25 NO_x molecules per ion pair [see *Porter et al.*, 1976; *Jackman et al.*, 1980]. This NO_x source did not perceptibly change either the NO_2 or the HNO_3 in the model computation. This NO_x source is concentrated in the lower stratosphere and upper tropospheric region at high latitudes (see Figure 13). The major contribution to NO_2 and HNO_3 in this region is from higher altitudes. Thus the GCR source is overwhelmed by the transported NO_x from other regions.

Building on the work of *Ko et al.* [1986], we have included lightning as a source of NO_x in the lower stratosphere at the low latitudes. We have used both the H4 and L4 lightning sources of *Ko et al.* The H4 source raises the NO_2 and HNO_3 in the lower stratosphere the most; however, we find that the model computation of nighttime $\text{NO}_2 + \text{HNO}_3$ is still about a factor of 2 lower than the LIMS nighttime $\text{NO}_2 + \text{HNO}_3$ in

this region. We thus require a NO_x source from lightning of the order of $6 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ between 4 and 15 km and between 30°N and 30°S to derive a NO_x that is similar to LIMS measurements in the lower stratosphere. This NO_x source from lightning is about a factor of 3 larger than that computed by *Tuck* [1976] and about 55% larger than that recommended by *Logan* [1983]. We want to emphasize that we are not precluding other sources besides lightning as possible candidates for the lower stratosphere NO_x source. Lightning is only discussed here as a proxy which would include any possible source of NO_x in the troposphere that could be transported to the stratosphere.

The computed HNO_3 in the polar latitudes is larger in the summer than in the winter, which is just opposite to the observations. A possible solution to this problem could be a change in the photochemistry. *Solomon and Garcia* [1983] and, more recently, *Evans et al.* [1985] suggested that N_2O_5 is converted to HNO_3 in the winter polar stratosphere by reaction with aqueous aerosol. Since our model does not include heterogeneous chemistry at the present time, we increased the $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ reaction rate by a factor of 100, from $2 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ (upper limit given by *DeMore et al.* [1985]) up to $2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$. We do not believe that this higher rate is correct but increase this as a proxy for a N_2O_5 reaction with aqueous aerosol. We find that by using this increased rate the computed HNO_3 in the winter is larger than the HNO_3 in the summer, in qualitative agreement with observations. This is best seen in Figure 14. Odd nitrogen is approximately conserved in the higher latitudes and in the middle to lower stratosphere; therefore the disagreements between our computations and the LIMS measurements suggest that some mechanism is necessary to create HNO_3 at the expense of N_2O_5 in the winter polar latitudes.

Austin et al. [1986] have recently performed a similar analysis, and their calculations indicate that the reaction rate for the $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ process need only be $2 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$. We find that use of this reaction rate leads to approximately equal amounts of HNO_3 in the winter and

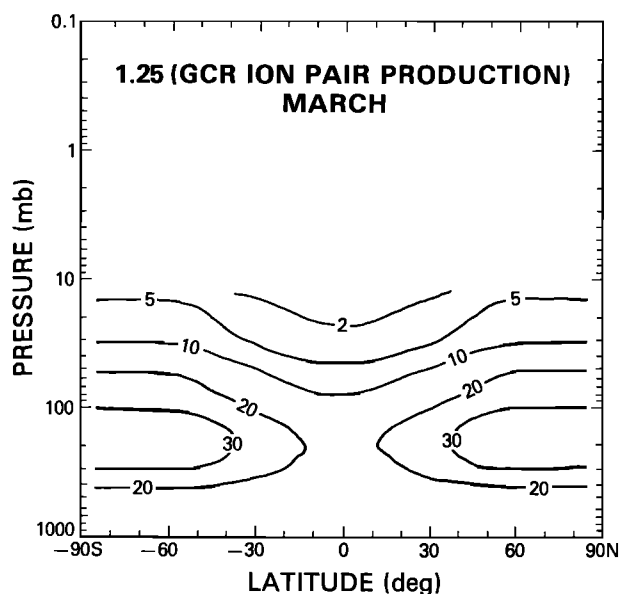


Fig. 13. Production of odd nitrogen due to galactic cosmic rays (in $\text{cm}^{-3} \text{ s}^{-1}$) for March 1979.

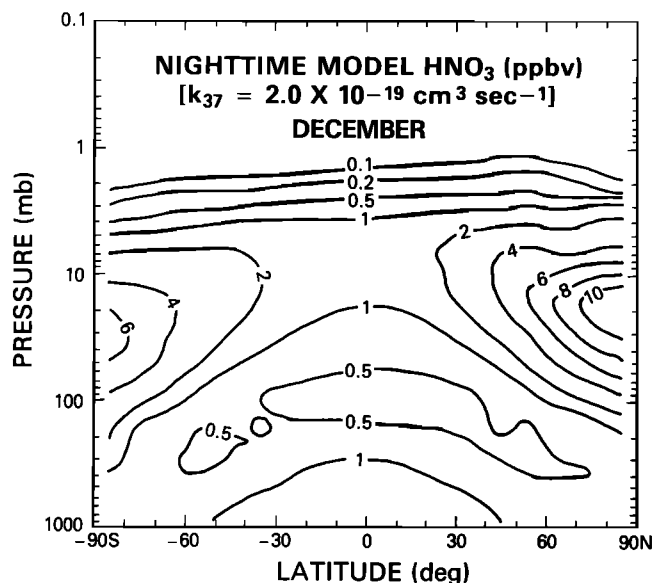


Fig. 14. HNO_3 distribution in December from model run with increase in reaction rate of $\text{H}_2\text{O} + \text{N}_2\text{O}_5$ by a factor of 100.

summer hemispheres. The LIMS data require more HNO_3 in the winter than in the summer hemisphere (see Figure 5b). These results would indicate a faster conversion of N_2O_5 to HNO_3 , more in line with the faster reaction rate of $2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ for $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ which was used in the computations to generate Figure 14. We should note that if the reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ is really occurring on aerosols, there will be only a limited spatial region (in both latitude and altitude) over which the process is important. This needs to be taken into account in future studies on the HNO_3 distribution.

Time constants (τ) for N_2O_5 reacting with H_2O for the three rates discussed above are given below for an altitude of about 30 mbar at high latitudes:

$$\begin{aligned} \tau &\simeq \text{years} & k_{37} &= 2 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1} \\ \tau &\simeq \text{months} & k_{37} &= 2 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1} \\ \tau &\simeq \text{days} & k_{37} &= 2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \end{aligned}$$

In order for the reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ to proceed with enough speed to have an impact, the time constant for the reaction must be less than months, probably of the order of a month to several days. Thus the reaction rate k_{37} should be $2 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ or slightly smaller. From our computations we find that there are still a few ppbv of NO_x tied up in the form of N_2O_5 at the very highest latitudes in winter even when using this faster reaction rate. This indicates that the differences observed in the NO_2 measurements of SME [Mount et al., 1984] where more NO_2 is observed on the east (downstream) side of wave troughs than on the west (upstream) could still be explained by the liberation of NO_2 from the residual N_2O_5 (left even after using the faster reaction rate) moving out of polar night to sunlit latitudes.

Since the peak of the measured HNO_3 is at a lower altitude than that from the computed HNO_3 , this suggests that downward motion may be stronger in the high latitudes in the real atmosphere than in the model used in these computations or that there is a problem in our understanding of the HNO_3 photochemistry of the stratosphere.

CONCLUSIONS

We have shown that there is broad agreement in the upper stratosphere, within the uncertainties of the calculation, between LIMS NO_2 and HNO_3 and those computed from a two-dimensional model computation with several species fixed. However, localized differences in the upper stratosphere and northern latitudes in the winter indicate that the NO_2 is not well understood in these regions. There are differences in the other parts of the stratosphere which indicate that there is another source of NO_x in the lower stratosphere at low latitudes, a possible candidate being a NO_x lightning source. The differences in HNO_3 between the measurements and the computations suggest that some chemistry transforming N_2O_5 to HNO_3 may be going on at high latitudes. There also is a discrepancy in that the calculated HNO_3 peak is at a higher altitude from that observed in the LIMS data.

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- P. D. Guthrie, C. H. Jackman, and J. A. Kaye, NASA Goddard Space Flight Center, Code 616, Greenbelt, MD 20771.

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